

PATENT SPECIFICATION

(11) 1 493 356

1 493 356

- (21) Application No. 57741/73 (22) Filed 13 Dec. 1973
 (23) Complete Specification filed 29 Nov. 1974
 (44) Complete Specification published 30 Nov. 1977
 (51) INT CL² C08J 9/28
 (52) Index at acceptance
 C3C 132 151 180 183 358 372 375 452

(72) Inventors JOHN ALISTAIR PARES, CHARLES WILLIAM
 ALFRED BROMLEY, PETER FRANCIS NICKS
 and PETER GEORGE OSBORN



(54) WATER-EXTENDED POLYMERIC MATERIALS

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, Imperial Chemical House, Millbank, London, SW1J 3JF, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to the formation of water-extended polymeric materials and in particular to the selection of certain surface active agents as emulsifiers for stabilising the emulsions used in their formation.

By the term water-extended polymeric materials we mean cellular structures of polymeric material filled, at least initially, with water or other aqueous liquid. They are made by emulsifying water or other aqueous liquid and a polymerisable water-immiscible liquid so as to form a reverse emulsion (i.e. an emulsion in which it is the aqueous phase which is dispersed in the organic phase; sometimes referred to as a "water-in-oil emulsion"), and then polymerising the continuous phase whilst maintaining the aqueous phase dispersed. The dispersed water droplets thus determine the cellular nature of the material and the size of the droplets determines the fineness of the cellular structure produced. For most applications the water or other aqueous liquid is removed after the polymerisation has been completed, and so throughout this specification, the term "water-extended polymeric material" is intended to refer also to the cellular polymeric material formed in this manner, whether or not the extending, i.e. cell-forming, water has been removed.

Various aqueous liquids have previously been described for use as the disperse phase of the water-in-oil emulsions, including water and aqueous solutions containing at least 40% water, previously disclosed solutes and admixed water-miscible liquids including lower alcohols, formamide, carbohydrates and inorganic salts. Similarly, the present use herein of such terms as "water-extended polymeric materials" and "water-in-oil emulsion" is intended to include the use of aqueous liquids containing dissolved or miscible substances

where the incorporation of water-soluble or water-miscible substances might be desirable, for example, the inclusion of water-soluble free acids is described hereinafter.

To form water-extended polymeric materials having an extension of at least 65%, i.e. materials formed from emulsions whose dispersed content of water or other aqueous liquid comprises at least 65% by weight of the emulsion, it is essential with most polymerisable liquids to use "sustained" emulsifiers capable of maintaining the stability of the emulsion at least sufficiently long (suitably 1 hour) to cover the period of the polymerisation reaction, and also of maintaining the water as the disperse phase during the polymerisation reaction until the continuous phase has solidified sufficiently to retain its shape, despite the changing composition of the mixture during polymerisation. If stability is not maintained during polymerisation, the emulsion either collapses, with the two phases either partially or wholly separating into distinct layers, or the emulsion inverts to an oil-in-water emulsion giving rise to a latex instead of a cellular material. This invention relates only to materials produced using the "sustained" emulsifiers described above (which indeed are fundamental to the production of any water-extended polymeric material having an extension of at least 65%); and processes which use as the sole means of stabilising the emulsion, surface active agents other than the above "sustained emulsifiers", form no part of the present invention.

The attainable droplet size of the emulsion is dependent on the efficiency of the emulsifier. Thus by using an efficient emulsifier a smaller droplet size, and hence a finer cell structure, can be obtained depending also upon other factors, e.g. agitation. Average cell diameters for such materials may be less than 10 μ m and with particularly efficient emulsifiers may even be sub-micron size. However the particularly efficient emulsifiers used for forming highly extended materials have hitherto always led to substantially closed cell structures. The use of an inefficient emulsifier, or the deliberate destabilisation of the emulsion before polymeri-

sation, have previously been suggested but this has led to low extension, i.e. less than 65% by weight. We have now discovered how to achieve substantially open pore structure at an extension of at least 65%.

In order to classify the cell structures of polymeric materials produced by polymerisation of the continuous phase of a reverse emulsion, we devised a test which was simple to carry out, and gave reproducible results which showed good correlation with photomicrographic evidence. To perform the test 400 g of a mixture of water and polymerisable liquid were emulsified to a reverse emulsion using an emulsifier as appropriate dissolved therein. A polymerisation initiator was added, and the emulsion transferred to a cylindrical mould of 6 cm diameter, the continuous phase then being polymerised. After completion of the polymerisation reaction, the resulting cylindrical block was transferred to a funnel having a cylindrical portion of the same diameter as the mould, so that it fitted closely around the block, and then the funnel was connected to an evacuating pump capable of reducing the pressure down to a value of about 22 mm mercury, for a period of 5 mins. By weighing the product before and after applying the reduced pressure, the weight of water lost was measured and expressed as a percentage of the weight of water present initially. This test, which is referred to herein as the Aqueous/Vacuum Test, gave a scale (the "AVT scale") which extended from about 80% (although higher values approaching 100% are theoretically possible) almost to zero.

We found that most products had a value on the AVT scale either within the range 0—5%, or 10—80%. All photomicrographs of materials having values within the range 0—5%, showed them to have a major proportion of closed cells. All photomicrographs of materials having values within the range 10—80% showed them to have a major proportion of open cells. The latter group may be subdivided, however. Most of them had values of 30—80% on the AVT scale, and there were only slight changes in appearance of the photomicrographs, all materials clearly being very open cell in structure. In the region 10—30% lay a minority of materials, and while the structures were clearly open cell from the photomicrographs, the inter-cell holes were visibly reduced, particularly at the lower end of the scale. These structures did behave as open cell structures in most respects and are encompassed by the invention defined below, but for consistency in properties associated with the openness of the cell structure, we prefer materials having values of at least 30% on the AVT scale.

Predried materials may also be tested for their AVT values, by soaking the material in water until the full amount of water has been taken up, and then applying reduced pressure

to a sample of the appropriate dimensions as before. With closed cell material it is often difficult to reintroduce the full quantity of water, but alternate low and high pressures during soaking may provide assistance. However, even when the full theoretical quantity has not been taken up, the water lost from materials treated in this manner, was found when tested to correspond fairly closely with the true AVT value provided it was expressed as a percentage of the theoretical quantity of water. This latter may be determined from the amount by which the density differs from the density of the same polymeric material in non-cellular form.

According to this invention, we provide a method for producing a water-extended polymeric material having an extension of at least 65% as hereinbefore defined and a value of at least 10% on the AVT scale as hereinbefore defined, comprising emulsifying to a reverse emulsion a mixture comprising at least 65% by weight of an aqueous liquid, a polymerisable water-immiscible ethylenically unsaturated liquid monomer and an emulsifier, and thereafter polymerising the continuous phase of the emulsion using a monomer-soluble initiator; wherein the emulsifier is an amphipathic material comprising at least one component solvated by the polymerisable water-immiscible liquid monomer and at least one other component solvated by the aqueous liquid, said component or components solvated by the polymerisable water-immiscible liquid monomer having a negligible reaction as hereinafter defined with the polymerising continuous phase and said same component or the overall balance of said same components being incompatible as hereinafter defined with the polymer formed, said amphipathic material being a randomised condensation product formed from reactants which comprise a polyfunctional acid, a polyfunctional alcohol and a water-soluble oxyethylated polyol.

Preferably the AVT value of the water-extended polythene material is at least 30%.

The invention further provides water-extended polymeric materials made by the above method.

It is preferred that the water-extended material has an extension of at least 75%.

Polymerisable water-immiscible ethylenically unsaturated liquid monomers which are suitable for use in the method of the present invention include for example acrylic and methacrylic esters and nitriles.

Whether open or closed cells are produced in the polymerisation reaction depends largely on the nature of the emulsifier components which are solvated by the polymerisable liquid monomer, and especially whether these components have negligible reaction with the polymerising mixture and/or are compatible with the polymer formed. These components may

be classified into three groups in respect of their reactivity towards the polymerising reaction mixture:

- (A) those that will copolymerise with the polymerisable liquid during polymerisation,
 (B) those that are completely inert or unreactive to the polymerisable liquid during polymerisation

- and,
 (C) those that undergo limited reaction e.g. by grafting, during the polymerisation.

Other factors (which may be related to those above) which may influence whether or not an open or closed cell structure will be formed, are the choice of initiator, the nature of the polymerisable liquid and the concentration of the emulsifier.

- Components that are of type (A) will always give closed cell structures irrespective of choice of initiator or polymerisable liquid, provided they do copolymerise with the polymerisable liquid of the continuous phase. Components of type (B) will always give open cell structures provided there is not a large excess of the emulsifier present. Components of type (C) are of intermediate reactivity between types (A) and (B) and may be used to give open or closed cell structures depending on the combined function of their reactivity and concentration.

In type (C) the reactivity results from the presence of labile hydrogen atoms in the molecules, typically arising from methylene groups adjacent to isolated double bonds or hydrogen atoms attached to tertiary carbon atoms.

The activity of these components may be predicted from published data (e.g. Rushman & Simpson, Paint Research Station Memorandum No. 217) on the α -methylenic activity of the individual component species.

For example the α -methylenic activities (Kr) of typical fatty methyl esters is as follows:—

	Kr
Palmitate (Saturated C_{16})	0
Oleate (monoethenoid C_{18})	0.081
9:12 Linoleate (diethenoid C_{18})	0.605
9:12:15 Linolenate (triethenoid C_{18})	1.10

When these fatty esters, or derivatives having equivalent carbon chains, are used in the formulation of emulsifiers, the relative reactivities of these chains are given by a comparison of their Kr values. Where mixtures of these chains are used, as found for example in the natural oils, the total activity of the mixture can be determined by adding together the contributions of each chain, based on its weight percentage of the mixture. Thus for example, for a natural oil comprising 50% by weight of a monoethenoid C_{18} ester, the activity contribution of that ester would be 50 % of 0.081, i.e. 0.041. To illustrate this, the total activities

of linseed oil and tall oil are calculated as follows:

	%	Activity Contribution	
Linseed—Saturated	10	0	
Monoethenic	22	0.018	
Diethenic	16	0.097	
Triethenic	52	0.572	70
Total Activity		0.687	
Tall—Saturated	8	0	
Monoethenic	46	0.037	
Diethenic	41	0.248	
Triethenic	3	0.033	75
Total Activity		0.318	

Where the linseed oil or the tall oil provides all the α -methylenic activity of the emulsifier, as in the alkyd-type emulsifiers described herein the calculated total activity of the oil gives the α -methylenic activity of the emulsifier. The calculated activities indicate whether or not an emulsifier molecule is likely to react with the polymerising reaction mixture. To obtain an indication of how much reaction there is likely to be between the emulsifier and the polymerising reaction mixture, an "activity index" (the product of emulsifier α -methylenic activity and concentration expressed as weight % of the polymerisable liquid at 80% extension) can be derived. We have found that with most polymerisable liquids (e.g. acrylic and methacrylic esters), there will be negligible reaction between the emulsifier and the polymerising reaction mixture when using hydrogen-abstracting initiators, only when the activity index is less than 0.13. This is understood to be the meaning of the term "negligible reaction" for the purposes of this invention. For example, the maximum quantities of linseed oil and tall oil which may be used if the polymeric material is to have the majority of its cells open, are 0.19 and 0.41% by weight of the polymerisable liquid, respectively (i.e. $0.13/0.687$ and $0.13/0.318$ respectively). As will be realised, these are the weights of the oils only, and not the weight of the whole emulsifier.

With polymerisable liquids that enter into grafting reactions particularly readily, to produce open cells, it may be necessary for the activity index to be zero, i.e. to use an emulsifier of type B.

Although for the production of open cells it may be necessary to restrict the activity index in this way when using hydrogen-abstracting initiators, such restriction is unnecessary where a non-hydrogen abstracting initiator is

used. In such cases, type C emulsifiers behave as type B. Examples of hydrogen-abstracting initiators include peroxides, hydroperoxides, peresters, monomer-soluble redox systems such as transition metal ion activated peroxides and electromagnetic radiation induced radicals such as those produced by gamma, ultraviolet and visible radiations. Examples of initiators which do not initiate hydrogen abstracting grafting reactions, include azo initiators such as azobisisobutyronitrile and 2,2 - azobisvaleronitrile.

During polymerisation, polymer molecules grow within the polymerisable liquid monomer. The component of the emulsifier which is solvated by the polymerisable liquid is also within the polymerisable liquid. Where the growing polymer and the polymerisable liquid-soluble component are compatible the two will coexist within the polymerisable liquid at all concentrations of the polymer. Where the polymer and the polymerisable liquid-soluble component of the emulsifier are incompatible, the emulsifier will be rejected by the polymer, forming a different phase. Whether or not the polymerisable liquid-soluble component of the emulsifier is incompatible with the polymer, is defined experimentally for the purposes of this invention by observing whether the partially or wholly polymerised liquid, when containing 10% by weight of the polymerisable liquid-soluble component of the emulsifier, has more than one phase at the polymerisation temperature, in the absence of the cell-forming aqueous liquid. The presence of a plurality of phases may be detected by turbidimetry where there is a refractive index difference between the phases. Where there is no such difference the plurality of phases may be indicated by the presence of a plurality of glass transition temperatures. These and other techniques for detecting the different phases are described by Sonja Krause in *J. Macromol Sci*, 7(2), 251-314 (1972), *Reviews in Macromol Chem*. Although the polymerisable liquid-soluble component will not normally be present in such high proportions, it is preferred that this proportion of 10% by weight of the polymerisable liquid be used when testing for incompatibility to increase the sensitivity of the test.

It is normal commercial practice, to use the minimum quantity of emulsifier which will produce the desired results, any excess being wasted raw material which reduces the efficiency of the process. It is assumed herein that such normal practices will be followed in carrying out the invention. The minimum quantity is specific to each set of materials and conditions, but fortunately it can be readily determined experimentally for each individual case. If sufficiently excessive quantities of emulsifier are used, however, in most instances the openness of the cell structure may be lost, even for the type B emulsifiers above. However, some guidance may be provided

in general terms. Thus although proportions of emulsifier as low as 0.02% by weight of the polymerisable liquid, may be sufficient to stabilise an emulsion comprising 80% by weight of water in methyl methacrylate when using the more efficient stabilisers described in the following Examples, high proportions of emulsifier may be required for maintaining higher water contents in a dispersed state, and when using the less efficient emulsifiers described therein. Even type B emulsifiers tend to produce closed cell structures when used in proportions much greater than 5%. However proportions of emulsifier less than 1% are generally sufficient for most emulsifiers. Proportions less than 0.5% are generally sufficient for the more efficient emulsifiers, and generally produce structures having the majority of their cells open, except for some emulsifiers having a high α -methylenic activity, when used with a hydrogen-abstracting initiator. Our preferred range of emulsifier proportions is therefore 0.02-5%, more preferably less than 1%, and especially less than 0.5% where the emulsifier is sufficiently efficient, all emulsifier proportions being expressed as percentages by weight of the polymerisable liquid, all upper limits being subordinate to the overriding factors described hereinabove pertaining to each individual situation, when open cell structures are required.

We have found that amphipathic materials which fall within the overall requirement for sustained emulsifiers generally require solvatable components which are large in comparison to the solvating molecules. This applies both to the components solvated by the aqueous liquid and to the components solvated by the polymerisable liquid. Thus for example, small hydrophilic groups such as isolated hydroxyl or carbonyl groups are by themselves insufficient as the sole water-soluble component of an emulsifier where high water contents are required, whereas the long chains of a water-soluble oxyethylated polyol such as polyethylene glycol, can be most effective. These solvatable components may be straight chain or branched.

Preferably, the component solvatable by the aqueous liquid, i.e. the water-soluble oxyethylated polyol should have a molecular weight of at least 400.

Suitable water-soluble oxyethylated polyols include polyethylene oxide condensates, either hydroxyl-terminated or methoxyl-terminated.

For the production of open cell structures, the component solvatable by the polymerisable liquid has to have negligible reaction with the polymerising reaction mixture and be incompatible with the polymer formed, in addition to its required solvatability as an anchor group of the emulsifier. Clearly, therefore, the selection will depend very much on the polymerisable liquid being used.

With reference to our earlier definition of incompatibility if the emulsifier incorporates several species of the above chain-like molecules as polymerisable liquid-solvatable components, it is not essential that every component be incompatible with the polymerising mixture, provided that the overall balance is one of incompatibility so as to provide the necessary rejection of the emulsifier during the reaction. Likewise mixtures of components selected from both groups may be used in a common emulsifier molecule provided the overall balance is such as to give sufficient solvation of the emulsifier molecule as a whole.

The emulsifiers used in this invention are randomised condensation products formed from reactants which comprise a polyfunctional acid, a polyfunctional alcohol and a water-soluble oxyethylated polyol, commonly termed alkyd resins. The component or components solvated by the polymerisable liquid will be contained in that fraction of the alkyd to which are linked the aqueous liquid-solvated residues of the oxyethylated polyol.

Our preferred emulsifiers are alkyds which are the reaction products of a polyol having a functionality greater than 2, a water-soluble oxy-ethylated polyol, a polybasic acid or its anhydride, and a monobasic acid having a carbon chain of at least 5 carbon atoms; and (as specified hereinabove) which have negligible reaction, if any, with the polymerising reaction mixture, and whose polymerisable liquid-solvated stabilising groups (i.e. groups other than the oxyethylated polyol) are incompatible with the polymeric material formed during the polymerisation of the continuous phase.

We have found that the more highly branched an alkyd the more effective it is as an emulsifier. The extent of branching may be controlled by choice of polyols and polyacids in formulating the alkyd. As a general guide, the simple relationship defining a theoretical critical gel point proposed by Kahn (J. Polymer Science 49, (152), Feb. 1961) may be used. Thus where

$$P_{OH}P_A = \left((f' - 1)(g' - 1) \right)^{-1}$$

P_{OH} being the probability that an OH group will react

P_A being the probability that an acid group will react

f' being the average functionality of molecules containing hydroxyl groups, and

g' being the average functionality of molecules containing acid groups.

A preferred alkyd emulsifier is one having a gelling structure, which occurs when the product $P_{OH}P_A$ is unity or less than unity.

Suitable polyols include glycerol and pentaerythritol, the latter being particularly useful in giving a highly branched alkyd. Equimolar

mixtures of pentaerythritol and glycerol are especially suitable.

The water-soluble oxyethylated polyol is preferably a polyethylene glycol. These are normally available as hydroxyl-terminated chains and it is by condensation of the terminal hydroxyl group that these molecules form part of the alkyd. However, they may be introduced into the reaction mixture in other forms which will produce the hydroxyl group in the reaction mixture, e.g. in the form of a hydrolysable ester. The most suitable molecular weights of the water-soluble oxyethylated polyol lie within the range 200—2000. Preferably the molecular weight lies within the range 400—1000. The quantity of oxyethylated polyol present in the alkyd is most suitably within the range 10—60% by weight of the alkyd, preferably within the range 20—60%.

The polybasic acid or its anhydride, may be for example a dibasic aliphatic acid such as adipic acid, or a dibasic aromatic acid such as phthalic acid, but acids having higher basicities, e.g. trimellitic acid, are preferred for the greater branching they produce. Mixtures of polybasic acids or their anhydrides may be used. The quantity of polybasic acid required depends on the quantities of the polyols and oxyethylated polyols used, since it condenses with these to form an alkyd according to the degree of branching.

Preferably the monobasic acid is a straight or branched chain C_{5-22} carboxylic acid. It may conveniently be a natural fatty acid (these generally being mixtures of C_{12-18} carboxylic acids) or oils based thereon.

The acid value of the alkyd is governed by the degree of conversion in the alkyd-producing reaction, and by the relative proportions of acid and hydroxyl groups present initially. Alkyds having acid values in the range 5—30 KOH/g are preferred.

We have also found that the emulsion may be more readily obtained by adding a small proportion, such as 0.5 to 5% by weight of the polymerisable liquid and suitably about 1.5 weight % of a free acid such as methacrylic acid, hydrochloric acid, oleic acid or acetic acid, the acids having the effect of reducing the viscosity of the emulsion. Such small proportions of acid have not been found to have any noticeable effect on the stability of the emulsion once it has been formed.

To avoid resistance to the opening of the cells during the formation of the cellular material, it is preferred that the polymerisation reaction be carried out at a temperature greater than the glass transition temperature of the emulsifier component which is solvated by the polymerisable liquid.

The water-extended polymeric materials of the present invention and the process for making them, may be used for most of the applications in which water-extended polymers are

already known. However they are particularly advantageous where the water is to be removed or where the open cell structure is required for other reasons. Thermoplastic water-extended polymers can be provided with a non-cellular skin by applying heat and pressure to the article (e.g. as described and claimed in British patent specification 1 360 397), and translucent or transparent panels may also be formed in sheets of the cellular material by fusion of selected areas (e.g. as described and claimed in United States patent specification 3 832 428). For example the skins may provide a durable and very attractive surface finish on a sheet of the material, for use as a kitchen work top, kitchen cabinet doors, front doors, bathroom tiles, coffee tables and other applications where a consistently smooth or textured surface is desired. The translucent panels may be formed to provide a front door with visual impact, for example, or to serve a utilitarian function in a display cabinet or illuminated sign. However, these fusion processes are not possible until the dispersed water has been removed, and the present methods, by providing a material having a majority of open cells, enables the water to be removed much more speedily and cheaply.

It is a feature of the emulsifiers described hereinabove, that they have negligible reaction with the polymerising mixture, and so they will not themselves cross-link the polymer molecules. Hence thermoplastic materials, such as polymethyl methacrylate, which would not otherwise cross-link, will not be caused to lose their thermoplasticity and hence their ability to readily form the skin and/or transparent panels. Other benefits accrue when the cabinet doors, table tops and other articles have to be transported, in that by removing the large proportions of dispersed water, the weight of the transported sheet or other article is very significantly reduced.

The polymeric materials may also be used as filtration membranes, thereby utilising the openness of their cell structures. By suitably selecting rigid or flexible materials, they may also be used in the preparation of bandages, upholstery or the formation of moulds for slip casting.

The invention is illustrated by the following Examples 7—51. Examples 1—6 are preparative and Examples 52—57 illustrate the stability of various emulsions. In these Examples the emulsions of Examples 7 and 10—57 were all of the "reverse" type. In all of the processes according to the invention the alkyd-type emulsifiers comprised residues of an oxyethylated polyol which were components solvated by water and the remainder of the alkyd molecule comprised a component or components solvated by the polymerisable ethylenically unsaturated monomer. The latter component or compo-

nents were also incompatible with the final polymer.

EXAMPLES 1—6.

Into methyl methacrylate as the polymerisable liquid, was dissolved 0.4 wt % of emulsifier and 1.5 wt % methacrylic acid, based on the weight of the methyl methacrylate. To 250 g of the resultant solution was added 750 g of water at 55°C, while the mixture was being sheared by a 27 mm diameter poppy head dispersator to form a water-in-oil emulsion. The water was added steadily over a period of about 10 sec, and the rate of shear kept low by rotating the dispersator at about 800 to 900 revolutions per minute. Shear rates much in excess of this were found to invert the emulsion to an oil-in-water type.

The prepared emulsion was split into two portions. The first portion was used to test the stability of the emulsion with time. It was examined visibly as soon as the emulsion was formed, and then set aside under ambient conditions, for 20 hours, after which time it was again examined.

To the other portion was added 1.5% by weight of t-butyl perpylvate, and the mixture poured into circular polythene moulds 4.25 inches (10.7 cm) in diameter and 2.5 inches (6.4 cm) deep. It was then placed in an oven at 50°C for about four hours to polymerise the methyl methacrylate. At the end of the four hours, the moulds were removed from the oven and their contents examined. Those which had successfully maintained their water in a dispersed state formed smooth surfaced, rigid blocks with water dispersed therethrough. In this test, emulsions when not effectively stabilised produce solid materials in various shapes and forms, all departing from the shape of the mould and thereby showing evidence of varying degrees of separation of the phases.

The blocks which were produced were then placed in an oven at 130°C to dry. These all appeared to have similar drying rates.

EXAMPLE 1.

An emulsifier was prepared by condensing pentaerythritol, polyethylene glycol 600 (i.e. polyethylene glycol having a molecular weight of approximately 600), trimellitic anhydride and tall oil, in the molar ratios 0.6/2.1/1.2/3. The resultant alkyd had an acid value = 19 mg KOH/g, viscosity = about 2 P, and % PEG (i.e. % polyethylene glycol, by weight) = 54.

The first portion quickly showed slight separation, but was still only partially separated after 20 hours. The polymerised portion produced a good block showing that the emulsion had been maintained during the polymerisation.

EXAMPLE 2.

An emulsifier was prepared by condensing pentaerythritol, polyethylene glycol having a

molecular weight of approximately 600—700, trimellitic anhydride and tall oil, in the molar ratios 0.6/2.1/1.2/3. The resultant alkyd had an acid value=8.2 mg KOH/g, viscosity—12 P and % PEG=54.

There was no initial separation of the emulsion. There was also no separation of the emulsion after 20 hours, but the structure appeared to be coarser than it did initially. The polymerised block was again well defined. The prepolymerised emulsion appeared to be more stable than that of the previous Example, and there was a noticeable difference in the appearance of the blocks, those of the previous Example having a coarser structure and more friable nature.

EXAMPLE 3.

An emulsifier was prepared by the condensation of pentaerythritol, polyethylene glycol 600, trimellitic anhydride and tall oil in the molar ratios 0.6/3.8/2.33/3.0. The resultant alkyd had an acid value—21.7 mg KOH/g, viscosity—35 P and % PEG=65.

There was no visible separation of the emulsion initially, but there was partial separation after 20 hours. However, the emulsion polymerised to produce a well-defined block.

EXAMPLE 4.

An emulsifier was prepared by the condensation of pentaerythritol, glycerol, polyethylene glycol 600, trimellitic anhydride and tall oil in the molar ratios 0.6/0.6/1.2/1.2/3. The resultant alkyd had an acid value=17 mg KOH/g, viscosity=10 P and % PEG=39.

There was no separation of the emulsion at any time during the 20 hours of the test, and the emulsion appeared to have a fine structure throughout. The block produced was well defined with smooth surfaces.

EXAMPLE 5.

An emulsifier was prepared by the condensation of pentaerythritol, glycerol, polyethylene glycol 600, trimellitic anhydride and tall oil in the molar ratios 0.6/0.6/1.2/1.2/3. The resultant alkyd had an acid value=17 mg KOH/g, viscosity=13 P and % PEG=40.

There was no visible separation of the emulsion at any time during the 20 hours. The emulsion polymerised to a well defined smooth-surfaced block indicating the efficiency of this alkyd as an emulsifier under these conditions.

EXAMPLE 6.

An emulsifier was prepared by the condensation of pentaerythritol, glycerol, polyethylene glycol 600, trimellitic anhydride and soya bean fatty acid in the molar ratios 0.6/0.6/1.2/1.2/3. The resultant alkyd had an acid value=21. mg KOH/g, viscosity=13 P and % PEG=40. This alkyd was essentially similar to that of the previous Example except that the tall oil was replaced by the soya bean fatty acid.

There was no separation of the emulsion even after 20 hours, but the emulsion appeared to be thinner and coarser than that of the previous Example. The block was again well defined and had a general appearance like that of the previous Example.

The polymeric materials of Examples 1 to 5 all had AVT values greater than 30%, and that of Example 6 had an AVT value greater than 20%.

EXAMPLE 7.

An emulsion was prepared using the mixture of Example 5 except that the weight ratio of water to methyl methacrylate was changed to 9:1, and the alkyd concentration increased to 2 weight %. While the poppy head dispersator was used to form the emulsion in the initial stages of water addition, a peristaltic pump with dropwise addition of the water was used when the emulsion became particularly thick, i.e. after about 80% of the water had been added. This produced a stable emulsion which was successfully polymerised and the water again readily removed. The material had an AVT value greater than 30%.

EXAMPLE 8.

The rates of drying of water-extended polymers prepared using the present alkyds as emulsifiers were compared with those of polymers prepared using other emulsifiers. We had found that the blocks of the previous Examples appeared to dry at approximately the same rate, and that of Example 4 was considered typical. Of the emulsifiers we had used previously, there did not appear to be any significantly different drying rates, and monomer-soluble ethyl cellulose was considered typical.

Two emulsions (A and B) were accordingly made, A being made as described in Example 4 and B being identical except that no methacrylic acid was added and the alkyd was replaced by 2% by weight of ethyl cellulose. These were placed in separate 3 ft square (91 x 91 cm) moulds such as might be used for forming cabinet door blanks, the moulds both being filled to a depth of 2.5 inches (6.4 cm), and the emulsions then cured in an oven at 50°C.

On removal from the oven, the blocks were removed from their moulds and placed in drying ovens maintained at 130°C. Block A appeared dry after about 2.5 days, but block B took a full 10 days to reach a similar state. This confirmed the impression we had obtained earlier when the smaller blocks of the previous Examples appeared to loose the bulk of their water remarkably quickly.

EXAMPLE 9.

Further drying tests were carried out using emulsions A and B of the previous Example. These were cast using cylindrical moulds of the kind used in Examples 1—6. The blocks

were placed in an evacuated chamber at room temperature, and weighed at intervals. It was found that the blocks made from emulsion A and using the present alkyd emulsion stabilisers lost 50% of their water after about 30 sec and 65% after about 5 min, whereas the blocks made from emulsion B using ethyl cellulose did not change significantly in weight.

Blocks A and B were later soaked in water and the water loss measured under the conditions of the Aqueous/Vacuum test. Block A gave a value of greater than 30% on the AVT scale and Block B gave a value less than 5%.

EXAMPLES 10—20.

These Examples are in the form of a series of experiments arranged to show the effect of concentration when using alkyds of differing unsaturation in their monobasic acid component, i.e. in alkyds having different degrees of reactivity towards the monomer used. Three alkyds were investigated, each being the reaction product of pentaerythritol, glycerol, polyethylene glycol 600, trimellitic anhydride and a monobasic acid in the molar ratios 1/1/2/2/5 (acid value 15.7 mg KOH/g), 1/1/2/2/5 (acid value 18 mg KOH/g) and 1.25/1.25/1.5/2/5 (acid value 27.6 mg KOH/g) for the three alkyds whose mono-

basic acids were respectively linseed oil, tall oil and capric acid. In Table I below the alkyds are identified by their monobasic acids. In each case the emulsion ingredients were:

methyl methacrylate stabiliser	80 parts by weight (various—as Table I)
demineralised water (pH 7.3)	320 parts by weight
benzoyl peroxide initiator	1.6 parts by weight

The stabiliser was dissolved in the monomer, then the water at 60°C was added and emulsified in an emulsifying apparatus in which the mixture was subjected to shear, the same degree of shear being applied to the mixtures in each experiment. The initiator was then stirred in, and the monomer polymerised at 60°C using a water bath. After polymerisation the degree of open cells in the structure was determined using the aqueous/vacuum test described hereinabove. The results are given in Table I, wherein the figures are the percentage of water removed during the Aqueous/Vacuum Test, the quantity of alkyd stabiliser is expressed as % by weight of the monomer, and the Examples Nos. refer to the experiments taken in order along their respective rows.

TABLE I

Example	% alkyd	% water removed		
		Linseed oil alkyd	tall oil alkyd	capric acid alkyd
10.—12	2.5	4.2	0.67	14.2
13—15	0.5	3.6	38.5	68.1
14	0.38	36.8		
17, 18	0.25	35.7		57.9
19, 20	0.12	31.8		38.4

Using the criteria described hereinabove to interpret these results (i.e. that for values above 10% indicate an open cell structure, and that values below 5 indicate a closed cell structure), it will be seen that an open cell structure can be obtained with all three alkyds, provided the alkyds are used in sufficiently small quantities. (All these alkyds are very efficient emulsifiers and no stability problems were encountered at any of the specified concentrations). However in concentrations beyond a critical concentration peculiar to the emulsifier (reached by only two of the three

alkyds tested) a closed cell structure results.

Further analysis shows that the critical concentration is related to the reactivity. The most unsaturated monobasic acid is linseed oil, with tall oil having approximately half the unsaturation of the linseed oil. The linseed oil alkyd reaches its critical point in this particular environment at a concentration of between 0.38 and 0.5% by weight of the monomer, whereas the tall oil alkyd does not reach its critical concentration in this environment until the concentration reaches about 1.5% by weight of the monomer. Thus the linseed oil

alkyd having approximately twice the unsaturation of the tall oil alkyd only requires about half the concentration of the tall oil alkyd before the closed cell structures are formed. Capric acid is saturated, and from these conclusions a capric acid alkyd would not be expected to reach a critical concentration. Indeed it does not form closed cells at any of the concentrations used in these tests, even at concentrations as high as 2.5% by weight of the monomer. However when used in even larger amounts, a concentration is reached even with the capric acid alkyd, when the excess emulsifier swamps the rejection effect of its incompatibility with the polymer formed in the reaction, resulting in a closed cell structure.

EXAMPLES 21—38.

These Examples form a further series, being a collection of experiments assembled to demonstrate the way in which an emulsifier, having negligible reaction with one set of polymerising reaction mixtures and producing open-cell structures with those mixtures, may

become reactive in a different environment, and produce closed cell structures. The emulsifiers selected were again alkyds these being incompatible with the polymer, so that the effects of changing the composition of the mixture may be limited to changes in reactivity. The alkyds were all reaction products of the following compounds pentaerythritol, glycerol, polyethylene glycol, trimellitic anhydride and monobasic acid in the molar ratios 1/1/2/2/5, except for Examples 31—34 in which the same compounds were reacted in the molar ratios 1.1/1.1/1.7/2/5. The monobasic acids were different, however, being selected to give a range of alkyds having differing degrees of unsaturation, and the procedure of the previous Examples 10—21 was repeated using a constant weight (0.4 parts by weight) of emulsifier. This represented 0.5% by weight of the monomer. The monomer was also varied to give environments of differing reactivities, and the cell structure was evaluated as before. Table II gives the results of these tests, the figures quoted being the percentage loss of water on the AVT scale.

TABLE II

Example	Alkyd		Monomers			
	Acid	AV	MMA	MMA + 10% 2-EHA by weight	St	BA + 5% EGDMA by weight
21 — 23	Oleic acid	26	11.7		3.0	73.6
24	Stearic*	26				75.4
25 — 28	Tall oil	18	38.5	40.4	1.6	68.1
29 — 30	Tall oil**	0			13.4	80.9
31 — 34	Lauric	25	52.8	59.7	55.2	74.2
35 — 38	Linseed oil	15.7	3.6	43.7	2.1	73.6

wherein AV = acid value (mgKOH/g)

MMA = methacrylate

2-EHA = 2-ethyl hexyl acrylate

St = styrene

EGDMA = ethylene glycol dimethacrylate

BA = butyl acrylate

* = alkyd of Example 21 hydrogenated

** = alkyd of Example 25 treated with diazomethane

EXAMPLES 39—42.

These examples form a series which illustrates how the reactivity of the emulsifier can be modified to provide open or closed cell structures. Example 39 is a "non-reactive" capric acid alkyd corresponding in formulation to Example 12. Example 40 was prepared by reacting the free carbonyl groups of the alkyd of Example 39 with glycidyl methacrylate (CMA) thereby converting it into a "reactive" emulsifier. Example 41 was a "reactive"

alkyd based upon dehydrated castor oil fatty acids (DCO) and prepared as in the previous series of examples. Example 42 was prepared from Example 41 to make it non-reactive by hydrogenation of the dehydrated castor oil component. (The latter failed to decolourise a solution of bromine in carbon tetrachloride thus indicating the loss of unsaturation in the alkyd.) The percentage water loss was again measured in the Aqueous/Vacuum Test, and the results obtained are set out in Table III.

TABLE III

Example	Alkyd acid	AVT
39	Capric	68.1
40	Capric + GMA	0.45
41	DCO	2.1
42	Hydrogenated DCO	52.1

These results illustrate how the material produced in the polymeric reaction becomes closed cell in structure when there is significant reaction between the alkyd and the polymerising mixture, and how an open cell structure may be obtained by selecting the stabiliser components so that for a desired monomer there will be negligible reaction.

EXAMPLES 43—51.

These Examples are in the form of a series of experiments in which different alkyds were used as emulsifiers for emulsions in which the polymerisation initiators were varied. The emulsions all consisted of methyl methacrylate (80 parts by weight), alkyd emulsifier (0.4 parts by weight), demineralised water of pH=7.3 (320 parts by weight) and polymerisation initiator (1.6 parts by weight). The emulsions were polymerised at 60°C as before,

and again the openness of the structure of the resultant polymeric material was tested by the Aqueous/Vacuum Test described hereinabove. Three different alkyds were used as emulsifiers, being those described in Examples 31, 25 and 35 respectively. These were selected again for this series of experiments as illustrating different reactivities, and are identified in Table IV below by their characterising acid. The different initiators selected were Perkadox Y16 (P-Y16) (Perkadox is a Registered Trade Mark) as a particularly active monomer-soluble initiator capable of causing grafting reactions by hydrogen abstraction, azo-valeronitrile (AVN) as a less active monomer-soluble initiator, and ammonium persulphate (AP) as a water soluble initiator. The results of these experiments are given in Table V below, the values quoted in Table V being the percentage water loss on the AVT scale.

TABLE V

Example	Initiator	Alkyd acid		
		Lauric acid	Tall oil	Linseed oil
43 - 45	P-Y16	52.8	38.5	3.6
46 - 48	AVN	39.6	31.6	44.1
49 - 51	AP	0.8	1.1	0.9

As shown in Table II, lauric acid and tall oil both give open cell structures with Perkadox Y16, and similar results are obtained with the azo-nitrile. This would be expected according to the above disclosure since the azo-nitrile would be unlikely to bring about significant reaction between the alkyd and the polymer-forming moieties where any such reaction had been negligible with the more active peroxide initiator. The water-soluble persulphate gives uniformly low AVT values indicating a need for initiation to take place within the bulk of the polymerisable medium.

EXAMPLES 52—57.

These Examples bring together various experiments to show the effect of branching in the molecule of an alkyd emulsifier and illus-

trate only the stability of various emulsions prior to polymerisation. In each Example the emulsion consisted of methyl methacrylate (80 parts by weight), alkyd emulsifier (0.4 parts by weight), and demineralised water of pH 7.3 (320 parts by weight). The water was added to a solution of the alkyd in the methyl methacrylate, and equal shear applied to the various mixtures to form the emulsions. The alkyd emulsifiers were the reaction products of pentaerythritol (PE), glycerol (G), polyethylene glycol (PEG) of molecular weight 600, trimellitic anhydride (TMA), adipic acid (AA) and a monobasic acid (MA) in the proportions (including absences) shown in Table VI below. Various monobasic acids were used, and these are identified in the table.

TABLE VI

Example	mono- basic acid	Alkyd						POH ^{PA}	Emulsion Stability
		molar proportions							
		PE	G	PEG	TMA	AA	MA		
52	tall oil fatty acid	1	1	2	2	0	5	0.69	Good
53	lauric	1.1	1.1	1.7	2	0	5	0.95	Good
54	tallo oil fatty acid	1.7	0	2	0	3	5	1.36	Poor
55	capric	0	2.75	1.5	2	0	5	1.13	Poor
56	capric	1.25	1.25	1.5	2	0	5	0.90	Good
57	DCO	0	2.33	2	2	0	5	1.15	Poor

wherein DCO = dehydrated castor oil fatty acid

"Good" indicates that the emulsion was stable for one week at ambient temperatures.

"Poor" indicates that the emulsion showed signs of breakdown after 1 hour (these alkyds were however found in further tests to be "sustained emulsifiers" as described hereinbefore (materials having an AVT greater than 10% being obtainable).

These examples show how the increased branching obtained by using a polyol of high functionality (e.g. pentaerythritol instead of glycerol) or by using an acid of high basicity (e.g. trimellitic anhydride instead of adipic acid) the stability of the emulsion may be improved.

WHAT WE CLAIM IS:—

1. A method for producing a water-extended polymeric material having an exten-

sion of at least 65% as hereinbefore defined and a value of at least 10% on the AVT scale as hereinbefore defined, comprising emulsifying to a reverse emulsion a mixture comprising at least 65% by weight of an aqueous liquid, a polymerisable water-immiscible ethylenically unsaturated liquid monomer and an emulsifier, and thereafter polymerising the continuous phase of the emulsion using a monomer-soluble initiator; wherein the emulsifier is an amphipathic material comprising at

least one component solvated by the polymerisable water-immiscible liquid monomer and at least one other component solvated by the aqueous liquid, said component or components solvated by the polymerisable water-immiscible liquid monomer having a negligible reaction as hereinbefore defined with the polymerising continuous phase and said same component or the overall balance of said same components being incompatible as hereinbefore defined with the polymer formed, said amphipathic material being a randomised condensation product formed from reactants which comprise a polyfunctional acid, a polyfunctional alcohol and a water-soluble oxyethylated polyol.

2. A method according to claim 1 wherein the AVT value of the water-extended polymeric material is at least 30%.

3. A method according to Claim 1 or Claim 2 in which the proportion of emulsifier lies within the range 0.02—5% by weight of the polymerisable liquid monomer.

4. A method according to Claim 3 in which the proportion of emulsifier is less than 1% by weight of the polymerisable liquid monomer.

5. A method according to Claim 4 in which the proportion of emulsifier is less than 0.5% by weight of the polymerisable liquid monomer.

6. A method according to any one of Claims 1—5 in which the emulsifier is the reaction product of a polyol having an average functionality of greater than 2, a water-soluble oxyethylated polyol, a polybasic acid or its anhydride and a monobasic acid having a carbon chain of at least 5 carbon atoms.

7. A method according to any one of claims 1—6 wherein the emulsifier has a gelling structure as hereinbefore defined.

8. A method according to any one of Claims 1—7 in which the polyol constituent of the emulsifier comprises a mixture of pentaerythritol and glycerol.

9. A method according to any one of Claims 1—8 in which the oxyethylated polyol has a molecular weight within the range 200—2000.

10. A method according to Claim 9 in which the oxyethylated polyol has a molecular weight within the range 400—1000.

11. A method according to any one of Claims 1—10 in which the quantity of oxyethylated polyol present in the emulsifier is within the range 10—60% by weight of the emulsifier.

12. A method according to any one of Claims 1—11 in which the oxyethylated polyol is a polyethylene glycol.

13. A method according to any one of Claims 6—12 in which the polybasic acid comprises trimellitic acid or its anhydride.

14. A method according to any one of Claims 6—13 in which the monobasic acid is a carboxylic acid having a carbon chain of 5 to 22 carbon atoms, or an oil based thereon.

15. A method according to Claim 14 in which the monobasic acid is a natural fatty acid comprising carbon chains of 12 to 18 carbon atoms, or an oil based thereon.

16. A method according to any one of Claims 1—15 in which the emulsifier has an acid value lying within the range 5—30 mg KOH/g.

17. A method according to any one of Claims 1—16 wherein the emulsion contains in addition to any acid reactant used in preparing the emulsifier, a free acid in a proportion within the range 0.5 to 5% by weight of the polymerisable liquid.

18. A method according to Claim 17 in which the free acid is methacrylic, hydrochloric, oleic or acetic acid.

19. A method for producing a water-extended polymeric material as claimed in Claim 1, substantially as hereinbefore described with reference to any one of Examples 7—51.

20. A water-extended polymeric material whenever made by the method claimed in any one of Claims 1—19.

21. A water-extended polymeric material according to Claim 20 whose average cell diameter is less than 10 μ m.

22. A water-extended polymeric material according to Claim 20 which is extended by at least 75%.

23. A water-extended polymeric material according to Claim 20, substantially as hereinbefore described and with reference to any one of Examples 7—51.

D. B. HALL,
Agent for the Applicants.